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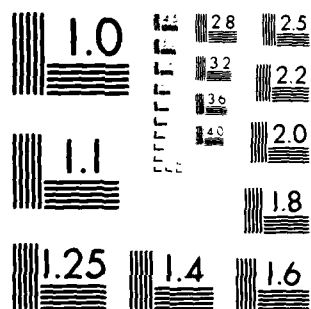
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SYMPOSIUM
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DISSERTATIONS ON CHEMICAL OCEANOGRAPHY

ABSTRACTS

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SYMPOSIUM ON
DISSERTATIONS ON CHEMICAL OCEANOGRAPHY

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**SYMPOSIUM ON
DISSERTATIONS ON CHEMICAL OCEANOGRAPHY**

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PREFACE

A continuing concern of the National Science Foundation (NSF), the Office of Naval Research (ONR), and the National Oceanic and Atmospheric Administration (NOAA) is the effective use of young scientists, who, in many instances, have gained their degrees through research supported by these organizations. These agencies are also interested in becoming more familiar with the ideas being formulated by individuals, who will be entering the field of oceanography and, independently, pursuing their research interests. It is important that these new graduates are in possession of the most recent information on the research climate and opportunities in their respective fields, are provided an insight into the structure and missions of the agencies involved, and are made aware of the procedures to follow in seeking support for research from these agencies. As a result, the Marine Chemistry Program of NSF and the Chemical Oceanography Program of ONR were extremely receptive to a suggestion made in October 1976 by E.D. Goldberg of the Scripps Institution of Oceanography that it would be useful to have a symposium convened that would be completely dedicated to soon-to-be or recent Ph.D. graduates in chemical oceanography. After discussions at some considerable length with members of the scientific community, preparations were set in motion for convening such a meeting, which was to be the first in a series.

The first Dissertations Symposium on Chemical Oceanography (DISCO) was convened in February 1978, being jointly supported by NSF and ONR. Subsequently, NOAA joined in cosponsoring the symposia, which have been convened at approximately 18-month intervals, with coordination being provided in all instances by the American Institute of Biological Sciences (AIBS).

During the week of March 5-9, 1984, the fifth DISCO was held at the East-West Center on the campus of the University of Hawaii at Manoa. In addition to the papers given by the invited participants, agency representatives made presentations on the respective missions of the sponsoring federal organizations and provided details on the paths to be followed in seeking support for research programs.

The abstracts of the papers given at the symposium which follow, present a wide range of information on geochemical, biochemical, and physicochemical processes in the ocean. The participants became very aware of the synergistic effect of close coordination between investigators in different disciplines. Relationships that were formed during the meeting should become instrumental in providing a new thrust on a large set of persistent chemical problems involving the ocean.

We feel the symposium was highly successful and look forward to results coming from the new professional bonds forged between the upcoming chemical oceanographers. We believe these enhanced professional relationships will facilitate future interdisciplinary and interinstitutional investigations. We also hope that the entire oceanographic community will become more aware of innovations in marine chemistry as a consequence of making the collective efforts of young workers more visible through such a symposium.

Our thanks go to Mary-Frances Thompson of the AIBS for providing the coordination necessary for this symposium to be successful. We thank also James P. McMahon for the superb meeting facilities at the East-West Center, and Steven V. Smith of the University of Hawaii for an enthusiastic and challenging address made to a most deserving group of young scientists.

Neil R. Andersen, NSF

Frank L. Herr, ONR

P. Kilho Park, NOAA

ABSTRACTS

SESSION I
AIR-SEA PROCESSES

AGRICULTURAL BURNING IN PANAMA AND CENTRAL AMERICA:
BURNING PARAMETERS AND THE COASTAL SEDIMENTARY RECORD

Daniel C. Suman

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Extensive tropical biomass burning in Panama and Central America produces large amounts of charcoal. A significant amount of this charcoal is deposited in the nearshore sediments through atmospheric transport and continental runoff. Sedimentary charcoal has been isolated from five sediment cores and their fluxes to the sediments determined. Particle-size distributions and morphologies shed light on transport mechanisms and on the types of vegetation burned on the adjacent land.

The Pb-210 chronology of the sediment cores was used to provide information on burning practices on the Isthmus, and the sedimentary record was compared with Isthmian anthropological and ecological histories. The relative uniformity of charcoal fluxes and particle morphologies during the past few centuries suggests that neither the land area burned nor the vegetation burned has significantly changed during this time frame.

The areal extent of land burned in 1981 in a region adjacent to the marine sediment cores has been determined. Dry deposition charcoal fluxes and aerosol charcoal concentrations during this same burning period were measured, and size-distribution analyses and morphological studies were performed on the samples. The data suggest that most of the sedimentary charcoal was transported by river runoff. The suspended load of charcoal in rivers may reflect decades of burning, which creates uncertainty in the sedimentary record. About 5% of the charcoal produced by biomass burning on the nearby land may eventually have a sink in these coastal sediments.

NITROGEN ISOTOPE STUDIES ON THE GEOCHEMICAL CYCLE OF N_2O

Naohiro Yoshida

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Physicochemical and biological reactions occur in the atmosphere. Nitrous oxide is one of the most important trace gases in the atmosphere because of its critical role in stratospheric chemistry and in the atmospheric energy budget. However, there are still many questions unanswered about the N_2O budget. Stable nitrogen isotope studies have clarified several major uncertainties about the global cycle of N_2O . The nitrogen isotope ratio of atmospheric N_2O is not determined by equilibrium isotope fractionations but mainly by kinetic isotope fractionations during production and/or consumption. As a result of this study, some important implications have been deduced about the geochemical cycle of N_2O : reduction of N_2O by microorganisms is the most important consuming process, nitrification plays an important role in producing N_2O , and the oceans are the net source for N_2O .

Equilibrium Nitrogen Isotope Fractionations (α_e)

α_e Between N_2O and Other Nitrogen Bearing Compounds. There have been no experimentally determined data available on α_e , except for theoretically calculated data by P. Richet (1976). According to Richet, $\delta^{15}N$ of N_2O is expected to be +28 per mil at 25°C, if N_2O is in isotopic equilibrium with atmospheric N_2 .

Reaction Rate of Isotope Exchange between N_2O and N_2 . ^{15}N -labelled species of $^{15}N^{14}NO$ and $^{14}N^{15}NO$ were prepared, individually stored with N_2 in the presence of other atmospheric constituents, and kept at 150°C and 200°C for 18 months. No isotopic exchange was observed between N_2O and N_2 . The N_2O was not in isotopic equilibrium with N_2 because the reaction rate of isotopic exchange was too slow to change $\delta^{15}N$ of N_2O during its atmospheric residence time (10-100 years).

α_e of N_2O Between Gas Phase and Aqueous Phase. α_e was determined by a solution experiment (in pure water, between 5°C and 25°C) to be 1.0007 to 1.0008, which is defined as $\alpha_e = (^{15}N/^{14}N)_{aq}/(^{15}N/^{14}N)_{gas}$.

Kinetic Nitrogen Isotope Fractionations (α_k)

General Description of α_k in Biological Reactions. Several important features of α_k in enzymatic reactions were derived from approximation treatments: closer values of α_k in enzymatic reactions to unity, rather than inorganic reactions; time course of α_k in enzymatic reactions; and the dependence of α_k on substrate concentrations. α_k was expressed in terms of the ratio of each reaction rate of each isotope: $\alpha_k = k_{14}/k_{15}$.

α_k During Denitrification ($\text{NO}_3 \rightarrow \text{N}_2\text{O}$). The α_k during denitrification was determined by the use of a pure culture of *Pseudomonas fluorescens* in 10^{-1} and 10^{-3} M NO_3^- . The result was consistently between 1.034 and 1.039.

α_k During Nitrification ($\text{NH}_4 \rightarrow \text{N}_2\text{O}$). The α_k , during nitrification by a pure culture of *Nitrosomonas europaea* was determined under several oxygen partial pressures to be 1.060-1.068.

α_k During Reduction of N_2O ($\text{N}_2\text{O} \rightarrow \text{N}_2$). The α_k during reduction of N_2O by a pure culture of *Pseudomonas denitrificans* was determined under several partial pressures of N_2O . The α_k changes from 1.005 to 1.027 corresponded to the change in the partial pressures of N_2O from 0.01 to 0.33 atmospheres.

α_k During Fixation of N_2O ($\text{N}_2\text{O} \rightarrow \text{N}_2, \text{NH}_3$). The α_k during fixation of N_2O by pure cultures of nitrogen-fixing microorganisms (e.g., *Azotobacter vinelandii* and *Anabaena cylindrica*) was 1.025-1.040.

Theoretical Estimation of α_k During Photolysis of N_2O . The α_k during photolysis of N_2O was estimated by regarding it as the same as that during N-O bond rupture of N_2O . It was estimated (using IR data of Begun and Fletcher, 1960, after Bigeleisen and Wolfsberg, 1958) to be 1.117 at 220 K, which is the representative temperature where photolysis of N_2O takes place.

Potential Activities of Soil and Sediment for the Reduction of N_2O

One of the uncertainties about the geochemical cycle of N_2O is the imbalance between production rate and consumption rate estimations. I focused on microbial reduction of N_2O as one of the most important consuming processes on the earth's surface. The measurement of potential activities of soil and sediment for the reduction of N_2O ($A_{\text{N}_2\text{O}}$), together with NO_3^- (A_{NO_3}), was done along a watershed of the Utsuchi River in Japan. $A_{\text{N}_2\text{O}}$ was measured using ^{15}N -labelled N_2O as a substrate. The change in $\delta^{15}\text{N}$ of N_2 in the gas phase linearly corresponded to $A_{\text{N}_2\text{O}}$. A_{NO_3} was measured by gas chromatographic determinations of N_2O , adopting the C_2H_2 -blocking method. Both activities were the highest in sediments at the seashore and in the bay. $A_{\text{N}_2\text{O}}$ was strongly correlated with A_{NO_3} . Further investigation of the $A_{\text{N}_2\text{O}}$ dependency on the partial pressure of N_2O , down to the natural level (3×10^{-7} atm) revealed that the dependencies of substrate concentration for both activities were identical to each other. This implies that microbial reduction of N_2O may be the most important consuming process on the earth's surface.

Nitrogen Isotope Ratio ($\delta^{15}\text{N}$) of N_2O in Nature

In the Lower Troposphere. The $\delta^{15}\text{N}$ s of N_2O collected from land surface air at three locations in Japan averaged 8.1 ± 1.0 per mil (32 samples). The $\delta^{15}\text{N}$ s of N_2O collected from maritime air over the Pacific Ocean (transpacific cruise of R/V *Hakuho Maru* averaged 7.2 ± 1.1 per mil (16 samples).

In the Upper Troposphere. The $\delta^{15}\text{N}$ s of N_2O collected by aircraft from the upper troposphere over Japan (altitude 0.70 to 8.39 km) averaged 11.3 ± 1.9 per mil (12 samples).

In the Ocean. The $\delta^{15}\text{N}$ s of N_2O dissolved in subsurface waters were measured in the eastern tropical Pacific Ocean. The $\delta^{15}\text{N}$ s of N_2O dissolved in the waters (where dissolved oxygen concentrations were more than 10×10^{-6} M) averaged 5.2 ± 1.3 per mil (6 samples). Those dissolved in the waters where the dissolved oxygen concentrations were less than 10×10^{-6} M, averaged 12.6 ± 1.1 per mil (4 samples).

Additional data for $\delta^{15}\text{N}$ of N_2O will be obtained from stratospheric samples (20 km) collected by balloon, from dissolved samples in seawaters of the northwestern Pacific Ocean, and from Lake Kizaki, where the enrichment of N_2O concentration is up to 200 times more than in the atmosphere.

Geochemical Cycle of N_2O Deduced From Nitrogen Isotope Data

On the basis of the data from this study, a box-model with three reservoirs (stratospheric, tropospheric, and oceanic) was constructed. Some important implications deduced from the model are as follows:

1. The N_2O in the stratosphere is highly enriched in ^{15}N in comparison to N_2O in the troposphere; the $\delta^{15}\text{N}$ of N_2O in the stratosphere is estimated to be 24 per mil.
2. Nitrification is one of the major producing processes for N_2O .
3. Microbial reduction of N_2O plays an important role in consuming N_2O .
4. The oceans are the net source for N_2O .

NITRATE AND NON-SEA SALT SULFATE IN AEROSOLS OVER MAJOR REGIONS

OF THE WORLD OCEAN: CONCENTRATIONS, SOURCES, AND FLUXES

Dennis L. Savoie

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About 900 bulk aerosol samples from major areas over the world ocean were collected aboard ships and at coastal land stations between 1979 and 1983, and were analyzed to determine the nitrate concentrations, non-sea salt (NSS) sulfate, sea salt, and mineral dust. These data, augmented with data from other workers, on several hundred samples were used to establish the geographical and temporal distributions of nitrate and NSS sulfate over the Indian Ocean, Red Sea, Mediterranean Sea, Atlantic Ocean, Gulf of Mexico, Pacific Ocean, and the East China Sea. Sixty, high-volume, cascade impactor samples (seven particle-size fractions) were collected at seven locations; these were analyzed to determine the particle-size distributions of nitrate, NSS sulfate, and sea salt in the maritime troposphere. Finally, 100 rainwater samples were collected on Virginia Key, a small island about five kilometers southeast of Miami, Florida. These were also analyzed for nitrate, NSS sulfate, and sea salt. The data from these samples and those from other workers were used to establish the relationship between the composition of rainwater and that of the ambient aerosols. All of the above information has been combined to estimate the fluxes of nitrate and NSS sulfate to the oceans, and to evaluate these fluxes in terms of the known and probable sources.

In all of the cascade impactor samples, the majority of the nitrate mass was found on intermediate size particles and exhibited a mass median diameter (MMD) of about 4 μm . The ratio of the MMD of nitrate to that of sea salt (about 7 μm) varied from 0.52 to 0.74; these ratios are similar to the ratio of the surface median diameter of sea salt to its MMD. The similarity of the ratios indicates that the nitrate mass distribution is well defined by the surface area distribution of the sea salt aerosols. The study further suggests that nitric acid vapor is rapidly removed from the marine boundary layer through adsorption onto, and reaction within, the sea-salt particles. The nitrate distribution contrasts sharply with the distribution of NSS sulfate (also produced from gas-to-particle conversion), which is present primarily on submicron aerosols.

Nitrate and NSS sulfate derived from continental sources (either natural or anthropogenic) have a significant and often substantial impact on the concentrations of the two constituents over vast areas of the world ocean. The impact of the continental sources is most evident in the northern hemisphere. In the landlocked seas and gulfs (Red Sea, Mediterranean Sea, Gulf of Mexico, and East China Sea), the mean nitrate and NSS sulfate concentrations range between 1.3 and 3.0 $\mu\text{g}/\text{SCM}$ (SCM = standard cubic meter) and between 2 and 10 $\mu\text{g}/\text{SCM}$, respectively. The maximum concentrations measured in these areas usually exceeded 5 $\mu\text{g}/\text{SCM}$ for nitrate and 10 $\mu\text{g}/\text{SCM}$ for NSS sulfate.

Over North Atlantic areas, downwind of North America and Europe, the nitrate concentrations average about 1 to 2 ug/SCM and the NSS sulfate concentrations average about 1.5 to 4 ug/SCM. Comparable means exist over the tropical North Atlantic during Saharan dust outbreaks; the high concentrations of nitrate and NSS sulfate during the outbreaks is a consequence of the transport of pollutants from Europe and North Africa. Continentally derived material also exerts a substantial influence on the concentrations of the two constituents over the northern Indian Ocean, especially near the Horn of Africa, and over the North Pacific in the region southwest of Mexico and Central America.

The mean concentrations in the northern portion of the Atlantic Ocean north-eastern tradewind regime and in the southern portion between Saharan dust outbreaks were relatively low: nitrate = 0.3-0.4 ug/SCM and NSS sulfate = 0.7 ug/SCM. However, even in these sets of samples, the possibility of a significant contribution from continentally derived material cannot be ruled out. These concentrations are comparable to those over the tropical and subtropical North Pacific during the high dust season from February through June. During the rest of the year over the north Pacific, the mean nitrate concentration may be as much as 20 to 30% lower; in contrast, the mean NSS sulfate concentration during the clean season is lower by about a factor of 2:0.3 ug/SCM.

Over the equatorial zone, the mean concentrations of NSS sulfate in the southeastern tradewind regimes of the Atlantic, Pacific, and Indian Oceans were all comparable to one another; the average in all three cases was about 0.5 to 0.6 ug/SCM. In contrast, the mean nitrate concentration (0.4 ug/SCM) over the Atlantic was about a factor of two higher than that over the Pacific and Indian Oceans. On the basis of models of NO production from lightning and dimethyl sulfide (DMS) emanation from the ocean, the nitrate concentrations over the Atlantic should be comparable to those over the other two oceans, and the NSS sulfate concentration over the Atlantic should be about a factor of two lower than that over the Pacific. The discrepancies between the models and the actual concentrations suggest that the transport from Africa may be a substantial impact on the concentrations in the southeastern tradewind regime of the South Atlantic.

Except near South America, the concentrations of nitrate are extremely consistent across the entire breadth of the tropical and subtropical South Pacific; the mean concentrations at all stations were within 20% of 0.08 ug/SCM. The mean NSS sulfate concentrations ranged from 0.2 ug/SCM to about 0.5 ug/SCM, possibly reflecting geographical variations in the primary productivity of the surface seawater.

Copper smelters are apparently a major source of sulfate and, to a lesser extent, nitrate in the region of southern Peru and northern Chile. The NSS sulfate and sulfur dioxide concentrations off the coast of southern Peru ranged up to over 20 ug/SCM and 15 ug/SCM, respectively; these values are comparable to those in heavily polluted urban areas. A substantially weaker, but still significant, continental source is reflected in the concentrations measured off the western coast of southern Africa.

The results from a preliminary evaluation of the rainwater data indicate that, at any given location, the NSS sulfate:nitrate ratio in rainwater is not

significantly different from that in the ambient aerosol. This suggests that the composition of rain is determined almost entirely by the simple washout of aerosols. The ratio of the concentrations in rain (in ug/ml) to those in air (in ug/SCM) is about 0.24 in Miami and about 0.16 at American Samoa. In contrast, the respective ratios for sea salt were 0.86 at both locations. The higher ratios for sodium reflect the enhanced production of sea salt during high velocity wind gusts associated with rain squalls.

Estimates of the deposition (total, wet, and dry) of nitrate and NSS sulfate are also in a preliminary stage. However, the nitrate concentrations in the southeastern tradewind regime over the equatorial Pacific and Indian Oceans and over the tropical South Pacific are in excellent agreement with those predicted from the geographical distributions of lightning and stratospheric sources of nitric oxide. In the same areas, the NSS sulfate concentrations are consistent with the estimated fluxes of DMS from the surface ocean.

METHYL IODIDE AND THE ATMOSPHERIC IODINE CYCLE

Eric L. Butler

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Recently, attention has focused on the possibility of methyl iodide (MeI) being the major component of iodine in air, and also as being the gaseous iodine species accounting for the preferential transfer of iodine (relative to chlorine or sodium) across the air-sea interface, and resulting in the enrichment of iodine in aerosols. MeI not only seems to play a central role in the geochemical cycle of iodine, but it may also play an important role in tropospheric photochemistry. Ozone concentration, OH radical abundance, and NO_2/NO ratio may be greatly affected by MeI.

A new procedure for the collection, analysis, and quantification of MeI in air samples was developed. Samples, collected by pulling air through Tenax filled glass tubes arranged in series, are sealed and returned to the laboratory for analysis. The collected vapors are thermally desorbed with continuous flow using a Tekmar LSC-3 purge and trap concentrator. The desorbed vapors are recondensed at the head of a 50m Silar 100C fused silica capillary column by immersing a portion of the column in liquid N_2 . Removal of the column from the liquid N_2 starts the gas chromatographic run; an electron capture detector is employed. Standardization is carried out by doping sampling tubes with known amounts of MeI prepared dynamically at low parts per trillion (ppt vol/vol) concentration levels and treating them in a manner identical to that of bonafide samples.

MeI samples have been taken over the course of one year at a coastal Rhode Island site. Concentrations of MeI varied between 0.28 to 2.2 ppt with a mean and standard deviation of 0.96 ± 0.86 ppt. The variability of MeI concentrations was mainly due to wind direction and time of year; on-shore winds had greater (2-4 times) concentrations of MeI than off-shore winds, and MeI was more abundant in spring and summer than in fall and winter.

Air samples were taken under well defined meteorological conditions for the analysis of total particulate iodine, total inorganic gaseous iodine, total organic gaseous iodine, and MeI. These samples were taken in the fall of 1982 on the windward side of Oahu and also at the Mauna Loa Observatory (MLU). The concentration of MeI at Oahu, representative of remote marine regions, ranged from 0.7 to 2.5 ppt; the concentration in downslope winds at MLU, representative of the free marine troposphere, was very low, less than 0.3 ppt. When comparing MeI measurements to concurrent measurements of other iodine phases, it was found that MeI can account for all of the total organic gaseous iodine. It comprises 25-37% of the total atmospheric burden of iodine.

SESSION II
CHEMICAL PROCESSES IN SEDIMENTS

THE GEOCHEMISTRY OF URCA BASIN SEDIMENTS

Der-Duen Sheu

Texas A&M University

The Urca Basin is a depression on the continental slope of the northern Gulf of Mexico, which is partially filled with anoxic hyper-saline brine. Steady-state diagenetic modelling of sulfate reduction in the basin sediments shows that sulfate reduction by sulfate-reducing bacteria is not inhibited by the high salt content of the basin water. Estimated rate constants of sulfate reduction range from 3.61 to $17.67 \times 10^{-12} \text{ sec}^{-1}$, where a simplifying assumption of a constant rate of sedimentation is used in the calculation. Thus, the rate of sulfate reduction is between $0.042 \exp(-0.0019)X$ and $0.203 \exp(-0.0093)X$ n moles S/ml brine/day, where X is the depth. The diffusion coefficients of sulfate ion in sediment interstitial water are estimated to range between 1.99 and $9.83 \times 10^{-6} \text{ cm}^2/\text{sec}$. All these figures are in good agreement with those reported in the literature for sediments deposited under normal saline conditions. However, the extent of sulfate reduction in the sediment is complicated and limited by reactions in the brine, which affect the nature of organic matter available to the sulfate-reducing bacterial community near and at the brine-sediment interface. Results show that only 20-30% of the total organic input is used by bacteria during sulfate reduction in the sediment, assuming no sulfide escaped from the sediments. Furthermore, the measured amount of solid-phase sulfide buried in the sediments shows that there is an appreciable amount of additional sulfide other than that accounted for by sulfate reduction in sediment interstitial water alone. This suggests that sulfate reduction occurs in the brine overlying the sediments and at the brine-sediment interface.

Sediments accumulated in this basin are intricately laminated on the mm to cm scale into visually highly color-contrasted layers. Studies of the chemistry of the sediments reveal that chemical diagenetic and physical sedimentary processes are important to the formation of this unique sediment deposit. Distinctively bright red layers enriched in hematite are found, which probably form during isolated incidences of enhanced mixing and oxygen supply across the normally stable brine-seawater interface. In contrast, the light gray, dark gray and black layers are enriched in sulfide, organic carbon and carbonate, relative to the red ones, and are deposited under strictly anoxic conditions. Analyses further suggest that the rhythmic occurrence of these anoxic layers may result from a fluctuation of primary productivity leading to a variation in organic matter input during deposition.

The distribution and partitioning of Fe and Mn into various components of the sediment units were determined using a chemical leaching scheme. Results show that Fe and Mn behave similarly in the Urca Basin and in other anoxic sediments, which have been discussed in the oceanographic literature.

A STUDY OF THE LOCAL AND REGIONAL CONTROLS ON THE COMPOSITION
AND MINERALOGY OF MANGANESE NODULES FROM THE NORTHEASTERN EQUATORIAL PACIFIC

Dan E. Olson

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Recent studies of oriented marine ferromanganese nodules have revealed significant textural and chemical differences between nodule top and bottom surfaces. These observations, together with sediment trap and pore fluid studies, strongly suggest some type of diagenetic input to the lower surfaces of nodules accreting in contact with the sediment. The different partitioning behavior of remobilized transition metals between sediment phases, nodule phases and sediment pore fluids may explain variations in the composition and mineralogy of that portion of nodules growing in contact with the sediment.

In order to separate the relative effects of local and regional scale factors, direct relationships between the chemistry of actively growing portions of nodules and their associated sediments were determined from a site in the siliceous ooze zone of the northeastern equatorial Pacific, MANOP Site S.

The outermost layers of polished nodule sections were studied by electron microprobe and scanning electron microscopy methods. The outer layers of the nodules can be divided by analyses into four distinct textural types, which can be related to nodule top or bottom surfaces. Oxide layers growing in contact with the sediment are characterized by columnar or disordered columnar textures, which are enriched in crystalline manganese oxides and in total Mn, Cu and Ni content. Parallel or wavy laminated textures are associated with nodule top surfaces, and are enriched in amorphous iron oxyhydroxides and in total Fe, Co and Ti content.

One Way Analyses of Variance (ANOVA) and multiple regression techniques were used to examine the dependence of the mean chemistry of each of the four textural types on several categorical variables, including topographic setting, sediment type and zone. Topographically, nodule samples were divided into three groups: (1) a northeastern plateau and ridge containing siliceous ooze; (2) valley floors containing thick sequences of reworked siliceous pelagic clay, and; (3) a southwestern plateau and seamount, with exposures of pillow basalts and sediments containing a thin sequence of siliceous pelagic clay overlying a nannofossil chalk ooze. Using associated sediment type, samples are categorized by siliceous ooze, siliceous pelagic clay, and siliceous pelagic clay with nannofossil chalk ooze. Zone, an arbitrary categorical variable, was established to describe changes in sediment type, nodule distribution, and topography over the study area.

The results show that total manganese, nickel, copper, and the Mn/Fe ratio increase in bottom textures from the southwestern plateau towards the northwestern plateau and ridge. This indicates a higher input of diagenetically remobilized transition metals into nodules associated with thicker sequences of siliceous sediment. There was no correlation between nodule top chemistry

with topographic setting or with sediment type. These results are in agreement with the model of Callender and Bowser (1980), which predicts that the ratio of manganese nodule/sediment accumulation rate for manganese increases in the order: pelagic clay, siliceous pelagic clay and siliceous ooze. This order apparently represents a gradient of increasing diagenesis.

Data on Ti and Fe/Ti ratios show a strong correlation with topographic setting and zone, but not sediment type. Lower Fe/Ti ratios in the southwestern plateau-seamount area suggest a local source for Ti enrichments, presumably from the weathering of pillow basalts.

When studying the variation in $Mn/(Ni + Cu)$ and $Ni/(Ni + Cu)$ ratios, there is no statistically significant relationship with depth, sediment type, topographic setting or zone. This result is in agreement with sediment extraction data in which the ratios of $Mn/(Ni + Cu)$ and Ni/Cu ratios in the sorbed fraction of the sediment also show no significant differences over the site. Using the model proposed by Lyle et al. (in press), comparisons of the flux of sorbed metal to the flux of dissolved species indicate that the pool of sorbed manganese, nickel and copper in Site K sediments is sufficiently large and rates of bioturbation are rapid enough for adsorbed metals to dominate the porewater reservoir in supplying metals for ferromanganese nodule formation. The fact that the ratio of adsorbed to dissolved flux rates for manganese, nickel and copper increase in siliceous sediments in the northeastern area of Site K, but ratios of these metals do not change in sediments and nodules, implies that local sediment factors, which control the degree of diagenesis, may control total metal accumulation rates in nodules. However, metal ratios may be predetermined by regional scale factors that affect the total supply of manganese, nickel and copper arriving at the seafloor.

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EARLY DIAGENESIS OF DEEP-SEA SEDIMENTS AND PALEOENVIRONMENT IN THE JAPAN SEA

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In order to reconstruct a geochemical history of marine basins from chemical records of bottom sediments, it is necessary to evaluate the diagenetic modification of the sediments. The objectives of this study are to clarify diagenetic processes occurring in deep-sea sediments of the Japan Sea and to reconstruct environmental changes in redox conditions of the bottom waters from vertical profiles of the sediments' sulfur content by considering diagenetic changes. The deep and bottom waters of the Japan Sea are highly aerated today, but there were anaerobic bottom waters during the last glacial period.

Four piston cores were collected from three deep-sea basins of the Japan Sea and interstitial waters, and were squeezed under air-tight condition at in-situ temperatures. Vertical profiles of pH, Eh, alkalinity, $\Sigma\text{H}_2\text{S}$, SO_4^{2-} , ΣNH_4^+ , ΣPO_4 , SiO_2 , ΣBO_3 , chlorinity, Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} , and Mn^{2+} were measured for the interstitial waters. Total sulfur, organic carbon, and the manganese content of the sediments were determined by porosity.

Porosity significantly decreased with increasing depth in the four cores. Sulfate concentration remarkably decreased in the interstitial waters of three cores, and hydrogen sulfide was observed in two cores, although the overlying bottom waters had been highly aerated. The Japan Sea may be the third deep-sea environment where sulfate reduction takes place within sediments, as in euxinic basins and continental slopes beneath the oceanic mid-water oxygen minimum. The interstitial waters of the four cores were classified into three types: (1) waters where alkalinity and manganese concentrations increase gradually with increasing depth in cores, and sulfate reduction is not appreciable; (2) waters where alkalinity increases with increasing depth in cores, sulfate concentration decreases remarkably, and hydrogen sulfide is not detected; and (3) waters where alkalinity increases with increasing depth in cores, sulfate concentration decreases remarkably, and hydrogen sulfide is observed.

Calcium and magnesium concentrations in the interstitial waters decreased with increasing depth, with a molar ratio of near unity. Calcium and magnesium content in 1N acetic acid-soluble fractions of sediment samples not containing foraminiferal tests (where interstitial and exchangeable ones were previously removed) increased with increasing depth, with a molar ratio of near unity. These facts suggest that calcium and magnesium have been removed from the interstitial waters through the diagenetic formation of Ca-Mg carbonate with a molar ratio of near unity.

In two cores collected from the Yamato (2970 m deep) and Tsushima (2360 m deep) Basins of the southern Japan Sea, where sulfate reduction is proceeding below the bottom surface, the total sulfur content of sediments gradually increases with increasing depth, showing several peaks. The sulfur is present mostly as framboidal pyrite spherules. The organic carbon content of sedi-

ments significantly varies with depth. A diffusion model, considering vertical change in the bulk diffusion coefficient of sulfate, gives the vertical profiles of diagenetically deposited sulfide-sulfur. The results indicate that the observed total sulfur content is composed of diagenetically deposited sulfide-sulfur, which increases gradually with increasing depth, and syngenetically deposited sulfide-sulfur, which forms the peaks over the diagenetically deposited sulfide-sulfur. The ages of the two cores were estimated from two known tephtras found in these cores. They were found to be between 12 and 31 kyr B.P., almost coinciding in age with the last glacial period.

In two cores collected from the Japan Basin (3540 and 3300 m deep) of the northern Japan Sea, the vertical profiles of total sulfur content (mostly present as framboidal pyrite spherules) are similar to each other, but are different from those of the Yamato and Tsushima Basins. The total sulfur content in both cases is less than 0.05% in the upper part, suddenly increases to 2.0% at certain depths, and reaches 5.0 to 4.2%. The vertical profiles of sulfate concentration in the interstitial waters and those of total sulfur of the sediments indicate that diagenetic deposition of sulfide-sulfur is not observed or not important in the two cores. These facts indicate that the extremely high sulfur layers of the two cores are due to syngenetic deposition of sulfide-sulfur as a result of the appearance of H_2S -bearing bottom waters. According to C-14 ages, the ages of the extremely high sulfur layers nearly coincide with the last glacial period.

The method developed makes it possible to distinguish between the amounts of sulfide-sulfur deposited diagenetically and syngenetically, and also to determine the appearance of H_2S -bearing bottom waters.

THE GEOCHEMISTRY OF TRACE METALS IN ANOXIC MARINE BASINS

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The zonation of geochemical processes operating in anoxic basins affords a unique opportunity to weigh the relative importance of these processes in the solid-aqueous phase partitioning and transport of metals across the oxygen-hydrogen sulfide interface. Two processes can be singled out as especially significant: the interface cycling occurring between metal oxides and their reduced dissolved phases, and the precipitation of metal sulfides in the presence of dissolved sulfide. Dissolved, and in some cases particulate, metal concentrations (Mn, Fe, Co, Ni, Cu, Zn, and Cd) were measured in anoxic basins of varying degrees of anoxic development. Conditions varied from Saanich Inlet, British Columbia, an intermittently anoxic basin with a seasonal oxygen-hydrogen sulfide interface at 150 m depth and maximum sulfide concentration of 20-40 μM , to Framvaren Fjord, Norway, a permanently anoxic basin with an interface at 17 m and sulfide levels up to 7000 μM in the deep water. The Cariaco Basin off Venezuela (interface at 300 m, maximum sulfide concentration of 50 μM) and Lake Nitinat, British Columbia (interface at 23 m, maximum sulfide concentration of 100 μM) represent basins of intermediate development.

The degree of involvement of these metals in the processes of interface cycling and metal sulfide precipitation follows class specific behavioral patterns and, in some cases, is related to the enrichment or depletion of individual metals in the sediments. The transition metals Mn, Fe, and Co show active involvement in interface cycling, characterized by a dissolved maxima just below the interface. Transition metal solubility in sulfidic waters is qualitatively consistent with predicted thermodynamic equilibrium trends. Manganese solubility is quantitatively consistent with thermodynamic equilibrium for a manganese sulfide of solubility lower than that of known phases. The Class B metals Cu, Zn and Cd display a dramatic solubility decrease across the interface, show no involvement in interface cycling, and are enriched in the sediments.

The speciation of dissolved metals in sulfidic waters is poorly known, largely due to the size and quality of the thermodynamic data base for metal-sulfidic ligand complexation. In order to characterize the solubility behavior of manganese and cadmium sulfides, and attempt to synthesize a low solubility manganese sulfide solid phase, a constant composition reaction vessel was constructed. Conditions will be monitored by pH and $pS^=$ electrodes and routine chemical analysis of total sulfide and metal concentration. Solid phases will be characterized by x-ray diffraction. The pH meter and an autoburet are interfaced to a minicomputer. Departures from programmed limits trigger the autoburet, which supplies stoichiometric quantities of reagents for reaction. The entire system is contained in an anaerobic chamber to minimize oxidative contamination.

BISMUTH, NICKEL, AND PALLADIUM IN NORTHEASTERN PACIFIC WATERS

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The marine geochemistries of bismuth, nickel, and palladium in northeastern Pacific waters were investigated with novel analytical methods.

The nickel determination method involved nickel carbonyl generation and atomic absorption detection. Dissolved nickel was reduced by sodium borohydride to its elemental form, which combined with carbon monoxide to form nickel carbonyl. The carbonyl was stripped from solution by an He-CO gas stream, collected in a liquid nitrogen trap, and then introduced into a quartz tube burner of an atomic absorption spectrometer (AAS). The concentration sensitivity of the method was $0.02 \text{ nmol Kg}^{-1}$, about 10^5 times lower than that of flame atomic absorption. A vertical profile similar to previously published ones was obtained with the method.

The method for bismuth determination involved bismuthine generation and atomic absorption detection. Dissolved bismuth was reduced by sodium borohydride to bismuthine, stripped with helium gas, and collected in situ in a modified carbon rod atomizer. The collected bismuth was atomized by increasing atomizer temperature, and detected by AAS. The detection limit was $0.015 \text{ pmol Kg}^{-1}$. Analytical results were obtained for natural waters, shells, marine algae and sediments. The vertical profile of dissolved bismuth in the northeastern Pacific was similar to that exhibited by manganese (that is, its surface enrichment, a secondary maximum at oxygen minimum depth, and deep depletion) implying their similar biogeochemical pathways.

The palladium analysis was done by graphite furnace AAS after two-step preconcentrations by anion exchange resin. The last step involved quantitative adsorption onto a single anion exchange bead, which was subsequently introduced and atomized in a graphite furnace. The vertical palladium profiles in seawater displayed nutrient-type surface depletion and deep enrichment. The concentration increased from $0.18 \text{ pmol Kg}^{-1}$ at the surface to $0.66 \text{ pmol Kg}^{-1}$ in deep waters. Like marine biogeochemistries between palladium and nickel were supported by their similarities in profile shape and oceanic residence time, and the fact that both exist in the dissolved state. Significant palladium enrichment in recent sediments from Palace Moat, Tokyo, Japan was observed and was, perhaps, a consequence of palladium usage in automobiles.

METHANE PRODUCTION AND SULFATE REDUCTION IN AN ANOXIC MARINE SEDIMENT

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This study is the first comprehensive examination of the depth distribution of rates of methane production and sulfate reduction, and the seasonal variability of these rates in an anoxic marine sediment. In organic-rich marine muds with high sedimentation rates, sulfate reduction becomes the principal electron acceptor for carbon oxidation, following exhaustion of oxygen, metal oxides and nitrate very near the sediment/water interface. In Cape Lookout Bight, North Carolina, the principal site for this study, dramatic sulfate depletion begins immediately at the interface with the 1 mM SO_4 isopleth, found at depths shallower than 10 cm in the summer and between 20 and 30 cm in the winter. In the surficial sediments (0-5 cm) the sulfate reduction rates typically range from less than 0.3 mmol SO_4 reduced $\cdot \text{l}^{-1} \cdot \text{d}^{-1}$ in winter to greater than 2.0 mmol SO_4 reduced $\cdot \text{l}^{-1} \cdot \text{d}^{-1}$ in summer. The latter rates are the highest ever measured in a "natural" marine sediment. For depths below the 1 mM SO_4^{2-} isopleth, new ion chromatographic techniques were developed and used to measure sulfate concentrations as low as 5 μM SO_4^{2-} in the high chloride marine environment, essentially two orders of magnitude less than the limit of the barium sulfate gravimetric method. This has allowed the accurate measurement of sulfate reduction rates at the interface between sulfate reduction and methane production.

Depth-integrated rates, determined by $^{35}\text{SO}_4$ tracer incubation, range seasonally from 6 to 70 mole $\text{m}^{-2} \cdot \text{yr}^{-1}$, agreeing well with modelled rates calculated from sulfate concentration gradients and independently determined apparent diffusion coefficients. The $^{35}\text{SO}_4$ tracer incubation rates agree to ± 25 -35% with rates determined by sulfate depletion in sediment packed tubes incubated and sacrificed over time.

Net methane production rates at different depths through the year were determined by the tube incubation technique. The maximum rates were found near the base of the sulfate reduction zone and ranged from 0.01 mmol CH_4 $\cdot \text{l}^{-1} \cdot \text{d}^{-1}$ in February to 0.26 mmol CH_4 $\cdot \text{l}^{-1} \cdot \text{d}^{-1}$ in August. Depth-integrated methane production ranged seasonally from 0.02 to 2.00 μmol CH_4 $\text{m}^{-2} \cdot \text{yr}^{-1}$, in close agreement with measured sediment-water total methane fluxes of 0.05 to 2.60 μmol CH_4 $\text{m}^{-2} \cdot \text{yr}^{-1}$, measured earlier at the same site. August methane production rates and depth distribution were also determined with ^{14}C -acetate and ^{14}C -bicarbonate. Again, maximum rates of 0.28-0.31 mmol CH_4 $\cdot \text{l}^{-1} \cdot \text{d}^{-1}$ were found near the base of the sulfate reduction zone. Some overlap of methane production from these tracers and sulfate reduction was observed.

SULFUR CYCLING AND THE SEASONAL SULFUR ISOTOPE DISTRIBUTION
IN AN ANOXIC MARINE SEDIMENT

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Seasonal variability in sulfur cycling and stable sulfur isotope distributions among porewater sulfate and sulfide, and solid-phase iron monosulfides and non-acid volatile sulfides (pyrite and elemental sulfur) have been investigated over a three-year period in the anoxic non-bioturbated sediments of Cape Lookout Bight, North Carolina. The study site is an end-member environment in terms of rapid rates of biogeochemical cycling processes associated with early diagenesis of organic matter. Sulfate reduction rates are among the highest reported for marine sediments and the sediment accumulation rate is approximately 10 cm/yr. The objectives of the study were to quantify the degree of sulfur isotope fractionation as sulfate reduction rates varied as a function of temperature, to use sulfur isotopes as natural tracers of processes of sulfide incorporation and recycling, and to distinguish between gross and net rates of sulfate reduction to establish an overall sulfur budget for the sediments.

Isotope fractionation between porewater sulfate and sulfide varied seasonally as a function of temperature and sulfate reduction rates. For example, during winter months at temperatures of 5-12°C, $\Delta\text{SO}_4\text{-HS}^-$ was 40‰ at sulfate reduction rates of 0.3 mM/day. During summer months at temperatures of 25-28°C and sulfate reduction rates of 1.1 mM/day, $\Delta\text{SO}_4\text{-HS}^-$ was only 20‰. Significant fractionation was found between the three reduced sulfur pools, with pyrite-elemental sulfur 10-20‰ lighter than iron monosulfides, and the latter 0 to 25‰ lighter than dissolved sulfide. This fractionation was determined to be due to greater rates of sedimentation in winter months as deduced from Be-7 data, and to sequential formation of the three pools of reduced sulfur in the newly arrived sediment as temperatures rose. In winter months, freshly produced dissolved sulfide reacted first to form elemental sulfur and pyrite in surficial sediments, followed by the formation of iron monosulfides in spring. During summer, concentrations of dissolved sulfide built up, reaching 8 mM by late August.

A sulfur burial rate of $15.5 \pm 3.1 \text{ moles} \cdot \text{m}^{-2} \cdot \text{y}^{-1}$ was calculated from the ^{210}Pb -derived sedimentation rate of $4.13 \pm 0.67 \text{ g} \cdot \text{cm}^{-2} \cdot \text{y}^{-1}$ and the asymptotic sulfur concentration below 30 cm depth of $12.0 \pm 1.4 \text{ mg} \cdot \text{g}^{-1}$ dry sediment. The annual sulfide flux out of the sediment was measured in anoxic benthic chambers and determined to be $5.4 \pm 1.4 \text{ moles} \cdot \text{m}^{-2}$; a net flux occurred during summer months only. Summing this flux with the rate of sulfide burial yields an annual rate of sulfide production of $21.1 \pm 3.4 \text{ moles} \cdot \text{m}^{-2}$, a figure that compares well with the seasonally averaged rate of sulfate reduction of $17.5 \pm 0.6 \text{ moles} \cdot \text{m}^{-2} \cdot \text{y}^{-1}$ determined from modelling porewater sulfate concentration data, and $22.8 \pm 6.1 \text{ moles} \cdot \text{m}^{-2} \cdot \text{y}^{-1}$ as determined by P.M. Crill (unpublished data) using radiosulfur techniques. Roughly 73% of the sulfate reduced

reacted to form iron minerals; 27% escaped and was reoxidized at the sediment water interface.

For comparison, sulfur cycling was also studied at a site located on the continental slope north of Cape Hatteras, in 500 m of water. The burial rate of sulfide in these heavily bioturbated, slowly accumulating (0.06 cm/yr) sediments is $73.4 \text{ mMoles} \cdot \text{m}^{-2} \cdot \text{y}^{-1}$, while the rate of sulfate reduction is $1179 \text{ mMoles} \cdot \text{m}^{-2} \cdot \text{y}^{-1}$. Thus, 94% of the sulfate reduced is reoxidized, and the net rate of sulfate reduction is 6% of the gross rate.

GEOCHEMISTRY OF THE SOUTHERN CALIFORNIA BORDERLAND BASINS;
CHEMICAL FLUXES FROM THE SEDIMENTS AND MIXING IN THE WATER COLUMN

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It is essential to understand the mechanisms and rates of dissolved substance exchange across the sediment-water interface for two reasons. Exchange across this interface is of major importance in controlling the water-column concentrations and speciations of several elements. Second, the flux of dissolved species across the sediment-water interface is a result of the depth integrated reactions occurring in the sediments. Thus, accurate estimates of benthic exchange are required for biogeochemical modeling of natural systems and also for interpretation of the sedimentary record. The research summarized below is directed towards quantifying sediment-water exchange rates for nutrients (silica, phosphate, nitrate), O_2 and CO_2 in several southern California borderland basins. The borderland, an area of moderate biologic productivity and with basins in varying water depths (800-2000 m) and varying distances from the coastline, provides a wide range of sediment and hydrographic conditions to study.

The first approach to this study of benthic exchange was an investigation of the distribution of radon-222 in the water column and sediments (to 40 cm) in the basins (Berelson et. al., 1982). Rn-222 (half life about 4 days) serves as a useful tracer for ocean mixing and sediment diffusion studies because its reaction sites and rates are known (as a product of Ra-226 alpha decay). Fitting the radon distributions in basin bottom water to a simple diffusion-reaction equation yields estimates of the vertical eddy diffusivity (k_z). Results from this model yield k_z values as follows: $2.5 \text{ cm}^2/\text{sec}$ in San Pedro Basin, $3.7 \text{ cm}^2/\text{sec}$ in Santa Barbara Basin, and $8.0 \text{ cm}^2/\text{sec}$ in Tanner Basin. A more sophisticated two-dimensional approach to modeling radon concentrations in the San Nicolas Basin gives a $k_z=17 \text{ cm}^2/\text{sec}$ and a horizontal eddy diffusivity of $10^5 \text{ cm}^2/\text{sec}$.

The nutrient/depth profiles in the basins have been modeled using the vertical eddy diffusivities derived from radon modeling and lower limit estimates of nutrient fluxes in and out of the sediments thus calculated. Fluxes in the San Nicolas Basin calculated this way (positive values for fluxes out of the sediments, negative into the sediments) are $46 \text{ nmole Si/m}^2\text{sec}$, and $37 \text{ Meq alkalinity/m}^2\text{sec}$. Fluxes in the San Pedro Basin are $15 \text{ nmole Si/m}^2\text{sec}$ and $33 \text{ Meq alkalinity/m}^2\text{sec}$.

The porewater composition in basin sediments (0-40 cm) is under study. Preliminary work with silica porewater modeling yields a silica flux from San Nicolas Basin sediments of $13 \text{ nmole/m}^2\text{sec}$.

The discrepancy between the silica flux modeled from water-column profile and porewater profiles is being studied by a third method of determining fluxes. Two benthic flux chamber/bottom landers, to be used to measure in-situ ex-

change rates, have been built. Experiments testing the effect of seawater on many different materials have been conducted to assure that composition changes measured during a flux experiment will be due to reactions between the sediments and overlying water and not with the chamber or sampler material. The field testing of these chambers thus far, has been successful. Cruises are scheduled in January and February 1984 to collect data from several basins. The radon fluxes calculated from the earlier radon modeling study will be used to measure the efficiency of these chambers.

This research contributes to the chemical oceanography community in several ways. The usefulness of Rn-222 as a tracer for water mixing on a complex coastal ocean setting has been demonstrated. This research will generate a model of silica and carbon cycles within these coastal ocean basins. In-situ benthic exchange rates will be compared to rates calculated from water column and porewater modeling. Studying nutrient exchange rates using independent methods will lead to a better understanding of the strengths and limitations of these methods.

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EARLY DIAGENESIS IN DEEP-SEA SEDIMENTS STUDIED WITH NATURAL RADIONUCLIDES

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Deep-sea sediments were collected from the northern North Pacific and the Bering Sea and separated into HCl soluble and HCl insoluble fractions. These sediments were analyzed for their uranium and thorium concentrations and U-234/U-238 activity ratios by alpha-spectrometry. The mean concentration of total uranium in the oxic northern North Pacific sediment was relatively low (1.25 ppm) and showed little variation with sediment depth. The concentration of total uranium in the surface sediment of the Bering Sea Basin was also low (0.85 ppm), similar to that of the northern North Pacific sediment, but higher (2.36 ppm) in the strongly reducing sediment below 40 cm. This increase in uranium concentration with depth is ascribed to higher quantities of HCl-soluble uranium. It is suggested that uranium diffuses through interstitial water and is postdepositionally precipitated during early diagenesis in the subsurface reducing environment. A postdepositional precipitation rate of uranium in the Bering Sea Basin sediment was estimated to be $28 \mu\text{g}/\text{cm}^2 10^3 \text{yr}$. In the reducing Bering Sea Basin sediment, the concentration of total uranium in the layers enriched in manganese carbonate was 1.68 ppm, which was slightly less than that of the other deep layer; this depletion of uranium may be due to dilution with volcanic material of coarser texture.

Sediment cores were taken with a box corer from the Japan Trench (water depth, 8260 m) and two neighboring shallower stations (water depth, 2970 m and 4310 m), and analyzed for uranium isotopes, thorium isotopes, Pb-210 and CaCO_3 . The Th-230/Th-232 activity ratios at the top layer (0 - 1 cm) are found to be 12 to 15 at all three stations examined, which means no appreciable addition of Th-230 during the fall through the water column below 4 km depth. There are also no significant differences in the concentrations of U-238, Th-232 and Th-230 on a carbonate-free basis among these three stations. The Th-230/Th-232 activity ratios of the Japan Trench sediments, from the top down to 30 cm, are nearly constant with depth, indicating either its rapid sedimentation or active vertical mixing of the sediments. The mixing depth of the Japan Trench sediments is estimated to be 7 cm from the vertical distribution of excess Pb-210. Moreover, the maximum concentration of Pb-210 in the Japan Trench sediment has not been found at the surface but at 2 to 3 cm depth. These results suggest that the sediment previously deposited on the shallower floor of the slope trench slides down and quickly accumulates onto the trench floor.

SESSION III

PROCESSES IN HYDROTHERMAL SYSTEMS

HYDROTHERMAL ACTIVITY IN THE GUAYMAS BASIN:
WATER COLUMN AND SURFACE SEDIMENT GEOCHEMISTRY

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Sea floor hydrothermal activity in the Guaymas Basin, Gulf of California, is quite different than that associated with ridge crest spreading centers. In contrast to these latter regions, thick sediments blanket the spreading centers in the Guaymas Basin and basaltic lava intrudes into this material, rather than extruding onto the sea floor. Percolation of hydrothermal fluids through the sediments radically alters their composition and mineralogy. These changes include the dissolution of diatoms and calcium carbonate, the recrystallization of smectite clays, and the precipitation of a host of sulfide, sulfate and silicate minerals. Mixing of seawater and hydrothermal fluids, which occurs at or just below the sea floor, causes the precipitation of anhydrite, barite, talc, and amorphous silica, and builds hydrothermal mounds and chimneys up to 30 m high.

Hydrothermal activity also has a very strong influence on the water-column chemistry in the Guaymas Basin. Injection of hydrothermal fluids occurs at the bottom of a semi-enclosed basin, and water column anomalies produced by this activity build up to much higher values than the open ocean. In the Guaymas Basin the hydrothermal venting generates large clouds of fine suspended particulate matter (SPM), 100-300 meters above active mounds and chimneys. These hydrothermal clouds have potential temperature anomalies of about 0.010-0.020°C, are enriched in dissolved silica, particulate and dissolved manganese, and depleted in dissolved oxygen, relative to areas away from the vents. The particulate manganese values increase from about 3nM/kg at about 1,000 meters, well above the enclosing topography of the subsill basin, to 100-150 nM/kg in the clouds of SPM and in the bottom nepheloid layer. The total Mn in the hydrothermal clouds (200-250 nM/kg) reveals a large component of dissolved Mn^{2+} , which diminishes with distance from active vents. The particulate Mn in the hydrothermal clouds appears to originate from direct precipitation of dissolved Mn^{2+} injected by the vents and entrainment of Mn-rich SPM in the rising hydrothermal plumes. Injection of silica-rich vent fluids into the basin bottom produces a silica anomaly of 10-15 μM , relative to the other deep basins of the Gulf of California. Spillover of Guaymas Basin deep water produces a silica plume just above the basin-sill depth, which is detectable to the mouth of the Gulf. A simple two-end member mixing model indicates that the deep waters of the Guaymas Basin contain approximately 0.1% hydrothermal fluid. Oxygen anomalies associated with the hydrothermal clouds are on the order of 5 μM , relative to regions away from active vents. The basin, as a whole, shows a depletion in oxygen of about 13 μM , relative to the other deep basins of the Gulf. This mixing model shows that this oxygen consumption can be explained by the oxidation of dissolved sulfide and methane injected by the hydrothermal vents. Box models of the deep basins of the southern Gulf of California indicate that the Guaymas Basin has a significantly higher source term for dissolved silica and sink term for dissolved oxygen

than the other basins. The calculated flux of hydrothermal fluids into the Guaymas Basin is $10\text{--}12\text{ m}^3/\text{second}$. This environment provides a unique opportunity to follow in-situ reaction rates and processes of oxidation, precipitation, adsorption, and biological uptake for non-conservative chemical species injected by the vents.

A detailed analysis of the major element composition of the SPM has been completed. The elements analyzed include Mg, Al, Si, P, S, Cl, Ca, K, Ti, Mn, Fe, and Ba. Four components constitute more than 90% of the weight of the SPM. These are diatom fragments, organic matter, clays, and manganese oxide minerals. In the water column well above the sill depth (1560 m), the first three components predominate, with MnO_2 constituting only 0.3% of the SPM. The MnO_2 fraction increases rapidly with depth below the basin sill and makes up to 15% of the weight of the SPM within the spreading troughs. The Mn/Al ratio increases from about 0.05 at 1,000 m to about 1.8 at 2,000 m. In the Farallon and Pescadero Basins, which are not hydrothermally active, the Mn/Al ratio increases to only 0.4 and 0.2, respectively. The much greater Mn/Al ratio in the Guaymas Basin is due to hydrothermal input. The ratio of Fe/Al in the Guaymas Basin (0.2-0.5) is about the same as in the other basins.

The differences between the Mn and Fe content of the SPM in the Guaymas Basin are consistent with the rapid oxidation kinetics of Fe relative to Mn. Any Fe injected by hydrothermal activity is rapidly oxidized and removed from the water column.

The much slower oxidation of Mn is demonstrated by the large increase in "dissolved" Mn in young hydrothermal clouds. Thus, Mn is distributed all over the deep basin by bottom currents before it is removed to the sediments. This process produces a Mn anomaly in the surface sediments of the spreading troughs. Reduction and mobilization in the anoxic basin muds, with oxidation and precipitation at the sediment-water interface, maintain this surface sediment enrichment even after hydrothermal activity shuts off. Thus, all of the basins of the southern Gulf of California show a Mn enrichment in their deepest parts.

Studies of sediment-hosted massive sulfide ore deposits have shown "halos" of Mn and other elements around the main ore bodies. It is likely that hydrothermal clouds like those observed in the Guaymas Basin are responsible for producing these "halos," which can extend several kilometers away from the ore body. Precipitation of Mn and/or Fe injected by venting activity will scavenge other elements from the water column. This particulate matter is removed from the water column by settling and adsorption onto other larger particles, producing an element gradient as one moves away from the main area of venting. Those elements not mobilized from the sediment by subsequent diagenesis leave a permanent record. The relative importance of Mn or Fe oxidation/precipitation will depend on the chemistry of the hydrothermal fluids and the Eh, pH conditions in the water column. In the Guaymas environment, Fe oxidation/precipitation and scavenging may produce sharp gradients very near vents, while the process for Mn may produce more gradual gradients over larger areas. Future work in the Guaymas Basin will establish the validity of this hypothesis.

CHEMISTRY OF SUBMARINE HYDROTHERMAL SOLUTIONS AT 21° NORTH,
EAST PACIFIC RISE AND GUAYMAS BASIN, GULF OF CALIFORNIA

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Submarine hydrothermal solutions at 21° north latitude on the East Pacific Rise were sampled for the first time in November 1979 and again in November 1981. In the 1981 program, four vent fields were sampled and a maximum temperature of 350-355°C was measured for three of the areas (OBS, SW and HG), and only 273° for the fourth area (NGS). The temperatures were stable over the 12 days of the diving program. The hot springs are "black smokers" that form the constructional features of Fe, Zn and Cu sulfides and Ca and Ba sulfates. The solutions are seawater that have been heated during convection through the oceanic crust and have reacted with basalt. The hydrothermal solutions are acid (pH = 3.3-3.8, 25°C, 1 atm), reducing (H_2S = 6.6-8.4 mmoles/kg, SO_4 < 1 mmoles/kg), and metal rich (Fe = 0.8-2.4 mmoles/kg, Mn = 0.7-1.0 mmoles/kg, Zn = 40-106 umoles/kg, Cu = 0-44 umoles/kg, Pb = 183-359 nmoles/kg, Co = 22-227 nmoles/kg, Cd = 17-180 nmoles/kg and Ag = < 1-38 nmoles/kg). Mg and SO_4 are quantitatively removed from these solutions while other elements are highly enriched. Li increases to 0.9-1.3 umoles/kg, K to 23.2-25.8 mmoles/kg, Rb to 27-33 umoles/kg and Ca to 11.7-20.8 mmoles/kg. Sr increases and decreases from the seawater concentration to 65-97 umoles/kg. Na and Cl also increase and decrease; the gain can be attributed to a ~7% loss of water due to rock hydration. Silica increases to 15.6-19.5 mmoles/kg and along the strike from the southwest to the northeast. Variations in other chemical components are not geographically consistent. Quartz geobarometry indicates a pressure of reaction between 300-600 bars, implying a depth of reaction within the oceanic crust of 0.5-3.5 kms, in agreement with the geophysical estimates. The silica data imply that the NGS vent is conductively cooling.

The Guaymas Basin, Gulf of California hydrothermal system was first sampled in January 1982. A total of 10 vent areas were sampled, with a maximum temperature of 315°C. In contrast to the 21° N systems where the solutions exit directly from basalt, the hydrothermal systems at Guaymas pass through and react with approximately 500 meters of sediment covered before they exit on the seafloor. This difference is reflected in the chemistry of the solutions. The sediment also provides a trapping mechanism for the metals in solution and a sediment-hosted type ore deposit may be forming at depth. These solutions differ from those at 21° N as they are less acid (pH = 5.9, 25°C, 1 atm), sulfur rich (H_2S = 3.8-6.0 mmoles/kg, SO_4 < 1 mmoles/kg) and metal rich (Fe = 0.02-0.18 mmoles/kg, Mn = 0.13-0.24 mmoles/kg, Zn = 0-40 umoles/kg, Cu = < 6 umoles/kg, Pb = 230-652 nmoles/kg, Ag < 230 nmoles/kg, Cd < 46 nmoles/kg, Co < 5 nmoles/kg). The higher pH and extremely high alkalinity (2.8-10.6 meq/kg) can be attributed to dissolution of $CaCO_3$ and thermal degradation of organic matter, which occur in the sediment column. The organic matter degradation is also responsible for the very high levels of ammonium (10.3-15.6 mmoles/kg) found in the solutions. The high pH and alkalinity are responsible for the

lower concentrations of the metals, which form insoluble sulfides. The ammonium exchanges for K and Rb in the sediments, raising their levels in solution to a maximum of 49.2 mmol/kg and 86 μ mol/kg, respectively. This is significantly higher than the values observed at 21° N. Li increases to 0.6-1.1 mmol/kg, Ca to 41.5 mmol/kg and Sr to 253 μ mol/kg. Na and Cl increase between 8-18%; this is attributed to hydration. Na is lost preferentially to Cl. Quartz geobarometry indicates a depth of reaction of ~0.5 kms into the oceanic crust.

These two sites demonstrate the importance of seawater reactions with basalt in altering the composition of seawater. The 21° N system is dependent only on reactions between seawater and basalt at elevated temperatures for its chemistry. The Guaymas system is a more complicated case in which reactions between the hydrothermal solutions and sediment overprint the basalt signature. The presence of large amounts of CaCO_3 and organic matter in the sediments at Guaymas is probably very important in determining the solution chemistry.

SESSION IV

MARINE ORGANIC CHEMICAL AND BIOLOGICALLY MEDIATED PROCESSES

AN INVESTIGATION OF THE INTERACTION OF *VIBRIO ALGINOLYTICUS*
AND COPPER IN NATURAL WATERS

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The form of trace metals in solution has been shown to be important in their interactions in physical and biological processes. Most trace metals are either toxic or essential to organisms; thus, metal-bacteria interactions should have an important effect on the form of the metal. Bacteria, because of their short generation time, are especially adept at modifying their environment. The aim of this research was to examine how bacteria modify the form of a particular trace metal, copper, in seawater.

Copper was chosen because it interacts with organisms as a nutrient and as a toxicant. Copper is present in seawater in several forms including free, complexed and particulate. The organism used in this study was *Vibrio alginolyticus*, a periphytic marine bacterial species commonly found in seawater. Initial experiments were made to determine what effect the copper had on the bacteria, and which forms of copper were involved. The effect of the bacteria on the form of copper in solution was subsequently studied.

The effect of copper on the bacteria was studied in aerobic and anaerobic cultures. Calorimetric, radiochemical and plate counting techniques were used to determine the effect of copper on heat production, respiration, carbon assimilation and the viable cell concentration of bacterial cultures. These techniques detected only a toxic interaction, which the culture was able to overcome after a lag period. Copper added as Cu(II) was more toxic to the cells in anaerobic culture than in aerobic culture. This increase in toxicity was attributed to a cytostatic effect seen only in anaerobic culture. The cytotoxic effect of copper was equivalent in aerobic and anaerobic cultures. The cytostatic effect, observed only in anaerobic culture, resulted in a decrease in the rate of metabolism of the surviving cells.

The effect of speciation on the toxicity of copper was examined by calorimetry. Inorganic and organic complexing was investigated, and the effect of organic speciation was tested with the chelators, EDTA and NTA. The complexes of copper with these chelators were not toxic to the bacterium. Inorganic speciation was determined using an ion-pairing model. The principal inorganic species of copper in seawater (carbonate and hydroxide) were examined. The carbonate complex was not toxic; however, the hydroxide complex was toxic. This suggests that bacteria do not simply respond to the thermodynamic copper ion activity, but that the kinetics of the complex are also important.

The effect of growth phase at time of initial exposure on the forms of copper in solution was examined. The effect of the time of sampling after exposure to copper on the copper was also studied. The different forms of copper investigated were labile soluble copper, non-labile soluble copper and particulate copper or copper associated with the cells. Labile copper was defined

as the electroactive copper measured by differential pulse polarography. The particulate or cell fraction was removed by centrifugation. The concentration of copper removed from the solution by the cells was 5 μ M. In all the experiments, the amount of copper associated with the cells was independent of growth phase at the time of exposure and of the time of sampling after exposure. This was attributed to saturation of surface cell sites. The soluble copper was primarily labile after initial exposure and shifted to non-labile as the bacteria recovered and started to regrow. In the death-phase experiments, the soluble copper was nearly zero in all the samples.

The results demonstrate that bacteria do affect the form of copper in solution. They remove a fraction of the copper from solution while complexing still more. The form of copper was also shown to be important in its interaction with bacteria and not simply related to the copper ion activity.

CHEMICAL STUDIES OF DISSOLVED CARBOHYDRATES IN SEAWATER

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Carbohydrates are one of the main components of organic matter dissolved in seawater and account for 10 to 20% of total dissolved organic materials. The chemical nature of the dissolved carbohydrates has rarely been characterized because of the lack of reliable methods for concentration and isolation. Elucidation of the chemical structure of the dissolved carbohydrates is necessary to clarify the biochemical significance of dissolved carbohydrates in energy metabolism of marine microorganisms. The aims of this study are to develop concentration and isolation procedures for dissolved carbohydrate, with sufficient quantities for structural analyses; to apply this method to various water samples to separate dissolved carbohydrates into mono-, oligo- and polysaccharides; to determine their chemical structures by the application of various chemical and physical methods; and, finally, to clarify the distribution and fate of dissolved carbohydrates in marine environments.

A combined charcoal column chromatography and dialysis system was developed for the concentration and separation of dissolved carbohydrates. This method was applied to water samples collected from Mikawa Bay, Japan (coastal areas), the Bering Sea, and northern North Pacific. Gas chromatography (GC), combined gas chromatography and mass spectrometry (GC-MS) and proton-nuclear magnetic resonance spectrometry ($^1\text{H-NMR}$) were used to elucidate chemical structures of saccharides isolated from seawater. Methylation studies were also conducted to determine linkage types of monosaccharide constituents of oligo- and polysaccharides from seawater samples.

The following results were obtained:

1. Combined charcoal column chromatography and dialysis was applied to water samples (2l for each of the water samples) collected from the coastal water. Mono-, oligo- and polysaccharides accounted for 7-9%, 15-26% and 27-43% of the dissolved carbohydrates, respectively. The polysaccharide was further fractionated to saccharides with M.W. <4,000 and M.W. >4,000 by Sephadex G-25 column chromatography.

2. Glucose, galactose, mannose, xylose, arabinose and ribose were found in the monosaccharide fraction, a neutral saccharide, with the concentration ranging from 0.2 to 40 $\mu\text{g/l}$. Almost the same order of magnitude of monosaccharide concentration was found in the Bering Sea and northern North Pacific.

3. Sucrose, laminaribiose, laminaritriose, raffinose and three glycerol glycosides (ranging from 0.5 to 27.7 $\mu\text{g/l}$ in water samples from the coastal water) were characterized by GC-MS and quantified by GC. Nuclear magnetic resonance spectrometry indicated that glycerol glycosides consisted of 2-O- α -D-glucopyranosylglycerol, 1-O- β -D-galactopyranosylglycerol and 6-O- α -D-galactopyranosyl-1-O- β -D-galactopyranosylglycerol. Sucrose, trehalose, melibiose and 1-O- β -D-galactopyranosylglycerol were also found in the water samples from the Bering Sea and northern North Pacific.

4. β -1,3 glucan (ca. 20 $\mu\text{g/l}$) was isolated from the polysaccharide fraction with M.W. >4,000 in the coastal water, and characterized by infra-red

spectrometry (IR) to determine steric configuration of the glucosidic linkage, and by methylation studies. Heteropolysaccharide (ca. 70 $\mu\text{g/l}$), consisting of glucose, galactose, xylose, fucose and rhamnose, was found in the polysaccharide fraction of M.W. >4,000, while a complex mixture of oligo- and polysaccharides were found in the polysaccharide fraction of M.W. <4,000. Thus, no further separation of saccharides was conducted. Heteropolysaccharide was found in water samples from the Bering Sea and the northern North Pacific in the range of 1 to 5 $\mu\text{g/l}$; no β -1,3 glucan was found.

5. Particulate matter from the coastal water, consisting of diatoms and flagellates as phytoplankton, was analyzed for these oligo- and polysaccharides. Laminarioligosaccharides and glycerol glycosides (mentioned above) as well as sucrose were found in the particulate matter, together with β -1,3 glucan and heteropolysaccharide.

These facts clearly indicate that cellular oligo- and polysaccharides once produced by diatoms and flagellates are easily released into seawater. When considering the high microbiological decay rates of these saccharides in natural waters, it can be seen that carbohydrates dissolved in seawater play an important role in the dynamics of organic matter in marine environments.

THE GEOCHEMISTRY OF ORGANIC CONTAMINANTS IN NARRAGANSETT BAY SEDIMENTS
AND THE AVAILABILITY OF THESE COMPOUNDS TO THE BLUE MUSSEL, *MYTILUS EDULIS*

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Many persistent organic contaminants accumulate to high concentrations in sediments of estuaries that are adjacent to urban centers. Due to the influence of organisms, currents, storms, dredging, etc., such sediments can become resuspended and transported in the water column. However, very little is known about the behavior of sediment-bound contaminants and their availability to organisms.

This study consisted of two major parts. First, the distribution of selected organic contaminants was investigated throughout the Narragansett Bay estuary. Surface sediments and sediment cores were collected along a transect from the head to the mouth of the bay. These samples were analyzed for total hydrocarbons, a suite of polycyclic aromatic hydrocarbons (PAHs), substituted benzotriazole compounds, and phthalic acid esters.

Results from this study indicated that all the compounds measured in surface sediments showed exponential decreases in concentration with distance down bay. The magnitude of the decrease did not appear to be directly related to the water solubility or *n*-octanol/water partition coefficient of the compound. Rather, the data indicate that these compounds are strongly bound to the sediment and a significant fraction does not freely partition between dissolved and particulate phases.

Sediment-core analysis indicated that diverse sediment depositional patterns occur within the bay. Contaminant profiles in the core from the upper portion of the bay show sharp demarcations, providing an historical record of input. In the sediment cores from the mid- and lower-bay locations, the input record is smeared, probably due to the influence of low sedimentation rates and active bioturbation.

For the second part of this study, contaminated sediment was collected from the head of Narragansett Bay and resuspended into a flowing seawater system containing blue mussels (*Mytilus edulis*). An air-lift siphon dosing apparatus, in conjunction with a transmissometer and microprocessor, was used to maintain constant particle levels in this system. The particle concentration in the exposure system was 14 ± 6.8 mg/l.

Several times during the experiment, the particulate and dissolved phases of both systems were analyzed for PAHs and polychlorinated biphenyls (PCBs). This was accomplished using glass fiber filters to retain the particles and polyurethane foam plugs to adsorb dissolved compounds. Analysis of foam plug and filter samples indicated that the dissolved and particulate phases contained markedly different contaminant profiles. In the dissolved phase only

low to medium molecular weight PAHs and PCBs were detected, compared to much wider distributions in the particulate phase.

Mussels were maintained in the exposure system for 40 days, then transferred to control seawater for an additional 40 days. During the exposure period, PAH compounds were quickly incorporated by exposed mussels. PAH concentrations and distributions in the dissolved and particulate phases of the dosing system were compared to those detected in the mussels. Comparing the n-octanol/water partition coefficients and bioconcentration factors in the mussels indicated that the dissolved phase may be the source of the 2-4 ring PAH compounds in the mussels. After transfer to control seawater, PAHs were rapidly depurated, with most following approximate first-order kinetics giving depuration half-lives ranging from 12-30 days.

Total PCBs were also quickly incorporated by exposed mussels; however, concentrations decreased slowly in mussels transferred to control seawater. The concentrations of specific PCB congeners in the mussels during the experiment are now being calculated. When this analysis is complete, PCB concentrations and distributions in the mussels will be compared to those measured in the dissolved and particulate phases of the dosing system.

REGULATION OF PHYTOPLANKTON CARBON AND NITROGEN PRODUCTION
IN THE DELAWARE ESTUARY

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Despite extremely large nutrient inputs from agricultural runoff and anthropogenic point sources, the Delaware estuary displays little evidence of noxious algal growth or severely depressed oxygen concentrations that characterize many eutrophic estuarine systems. This research was initiated to examine the relationship between phytoplankton production and nutrient distributions in the estuary, with specific emphasis on: (1) determining what factors regulate production in the presence of non-limiting nutrient concentration, (2) assessing the overall rates of carbon and nitrogen production in the estuary and resolving the relative importance of specific inorganic nitrogen species to production, and (3) defining the relationship between fresh-water nutrient inputs and production rates in the system. Data were collected along the entire salinity gradient of the estuary (0-31‰) during 19 cruises of the *R/V Cape Henlopen* between October 1980 and January 1983.

Chlorophyll concentrations were found to be regulated by light availability in the surface mixed-layer. Observed distributions were correctly predicted using a steady-state light-limitation model in which suspended sediment concentration, depth of the mixed-layer, and ambient light intensity were the primary model parameters. In spring, chlorophyll concentrations reached 50-60 $\mu\text{g l}^{-1}$ during a *Skeletonema costatum* bloom centered in mid-estuary. Spring and transient fall blooms (15-20 $\mu\text{g l}^{-1}$) were focused in mid-estuary due to settling out of suspended sediments below the turbidity maximum and physical factors that caused vertical stratification in that region. In summer, despite higher ambient light intensities, chlorophyll concentrations in the lower estuary remained below 10 $\mu\text{g l}^{-1}$. These low concentrations appear to be regulated by a combination of light-availability and grazing. As a result of high turbidity in the upper estuary, and a deep mixed-layer in the mid- and lower estuary (except during periods of vertical stratification), accumulation of algal biomass in the Delaware estuary remains below the nuisance levels found in many other nutrient-rich systems.

Carbon production in the estuary averaged 228 $\text{gm C m}^{-2} \text{ year}^{-1}$ for 1981 and 1982. Spatial patterns of daily areal production (*SP*) in the upper estuary paralleled chlorophyll concentration, ranging from a maximum of 1.1 $\text{gm C m}^{-2} \text{ d}^{-1}$ during summer to a minimum of <0.1 $\text{gm C m}^{-2} \text{ d}^{-1}$ in winter. In the mid- and lower estuary, maximum *SP* occurred during two periods: during summer under low phytoplankton biomass (2-10 $\mu\text{g Chl l}^{-1}$) at the estuary mouth (3.1 $\text{gm C m}^{-2} \text{ d}^{-1}$), and during the spring bloom in mid-estuary (2.5 $\text{gm C m}^{-2} \text{ d}^{-1}$). Despite the occurrence of the highest nutrient concentrations in the fresh-water region, 90% of the annual production occurs in the lower estuary. The presence of the turbidity maximum immediately downstream from major nutrient point sources in the Philadelphia metropolitan region delays production and buffers the influence of the nutrient addition.

Specific nitrogen uptake and ammonium remineralization were examined using ^{15}N uptake and isotope dilution techniques. Maximum nitrogen uptake ($>380 \text{ nmol N l}^{-1} \text{ h}^{-1}$) occurred during summer, and was related primarily to water temperature. Ammonium fulfilled 82% of annual phytoplankton nitrogen demands, despite a dominance of NO_3^- in the ambient dissolved inorganic nitrogen pool. Ammonium concentrations in excess of $1\text{--}2 \text{ }\mu\text{M}$ generally suppressed NO_3^- assimilation; however, this suppression was not as universal as has been reported for other systems. The presence of extremely high NO_3^- concentrations (often $100\text{--}200 \text{ }\mu\text{M}$) and advection of NO_3^- adapted coastal populations into the estuary are suggested as possible explanations. Nitrate was a significant source of nitrogen only during high production in summer, and under low NH_4^+ concentrations towards the end of the spring bloom.

Despite anthropogenic nutrient inputs that are among the highest measured for estuaries in the United States and light-limitation of phytoplankton growth, phytoplankton nitrogen demands in the estuary exceeded nitrogen inputs. Nitrogen flux into the lower estuary was modeled using a steady-state advection-diffusion model and compared with measured phytoplankton uptake rates and changes in dissolved inorganic nitrogen (DIN) pool. During spring, uptake in the lower estuary ($142 \text{ mols N sec}^{-1}$) was balanced by a loss from the DIN pool and input from upstream. During late fall, uptake and flux were in approximate balance. In contrast, summer phytoplankton demand for ammonium ($239 \text{ mols sec}^{-1}$) was far in excess of fresh-water input. This ammonium deficit was primarily fulfilled by water-column ammonium remineralization from the micro-heterotrophic fraction ($<20 \text{ }\mu\text{m}$) that was found to supply between 48 and 134% of phytoplankton nitrogen demands. Maximum remineralization rates reached $398 \text{ nmole N l}^{-1} \text{ h}^{-1}$.

The apparent paradox, in which ammonium remineralization is required to fulfill phytoplankton nitrogen requirements despite non-limiting nitrogen concentrations, is explained by examining uptake and remineralization rates, and phytoplankton NH_4^+ preference. The results show that high levels of nutrient input should not be considered a-priori evidence of 'eutrophic' conditions. The interaction between nutrient distribution and phytoplankton processes must be assessed by examining the complex relationship between estuarine physics and chemistry, and phytoplankton physiology.

THE GEOCHEMISTRY OF METAL-ORGANIC COMPLEXES AND
NUTRIENT-ORGANIC COMPONENTS IN NARRAGANSETT BAY POREWATERS

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Organic matter in seawater has the ability to form complexes with a variety of metals. These complexes influence the chemical speciation of the metal and can alter its geochemical behavior (e.g., net transport, adsorption-desorption reactions, toxicity and solubility). Nutrients, such as nitrogen and phosphorus, may also be combined with organic matter. However, the amounts of these components formed, the variation in the extent of association with organic matter, and the source of organic matter in different marine environments are poorly understood.

Estuarine sediments are major sources and sinks for a variety of organic and inorganic compounds; the fate of these compounds, once they enter the sediment, is uncertain. These marine sediments provide a natural laboratory in which large geochemical changes occur within the upper 20 cm of the sediment column due to the anoxic decomposition of organic matter. The response of the organic components to these changes and to variations in the inorganic forms provides an improved understanding of the chemical nature of these components and their possible role in the transport to and from the benthos.

This study had four phases: (1) To determine if dissolved organic components of copper, nitrogen, and phosphorus are present in the interstitial waters of Narragansett Bay sediments, as measured by C_{18} reverse-phase chromatography. (2) To observe the distribution of these organic-components with total copper, DON, DUP, DOC, H_2S , pH, Eh and depth in the sediments. (3) To follow the transport and distribution of copper and its organic components in the sediments during a large scale copper addition experiment, within four microcosms, at the Marine Ecosystems Research Laboratory (MERL). These systems were part of a two-year study in which nutrients N and P were continuously added to each tank in various quantities (1-32x bay concentration) to observe the effect of eutrophication on the marine chemistry of the system. (4) To characterize partially the specific organic components by isotope ratio mass spectroscopy, ESR, and HPLC.

Overall, the isolation procedure recovers 21-29% of the porewater DOC, 60-100% of the total copper, 11-75% of the DON and measurable amounts of the DUP.

Organic copper exhibited a seasonal and depth distribution. Generally, the highest organic copper values were isolated from the upper 3 cm of the core. This value appeared to vary from winter to summer (5 nmol/kg, winter; 13 nmol/kg, summer). This is not unexpected due to the increased particle flux to the sediments during the summer, and subsequent release of organic copper to the porewaters. The surface porewater and overlying water organic copper concentrations were essentially the same (13 nmol/kg surface porewater versus

11 nmol/kg in overlying water) and decreased with depth in the core (3 nmol/kg at 20 cm).

The amount of organic copper present in the porewater was not directly correlated to the porewater DOC concentration and, thus, is related to the qualitative nature of the DOC, rather than the quantity of DOM present. DOC was correlated with DON and DUP.

The effect of porewater pH changes on the distribution of organic copper in the sediments is complicated due to competing effects of sulfides and Eh changes. A model is presently being developed to determine the relative importance of the measured geochemical parameters on the distribution of organic copper in the porewaters.

Results from the MEKL copper addition experiment suggest that organically-complexed copper is rapidly formed in the water column upon addition of inorganic copper. These increased overlying water levels subsequently result in a 20% increase of organic copper in the porewaters within one month after the initial addition. This indicates that the organic-copper species may be important as a transport mechanism for copper in the marine environment.

Collection and interpretation of the organic-component structural information is still in progress. Analysis of this information will provide an insight into the source, role and fate of these organic components in the marine system.

THE BIOGEOCHEMISTRY OF MANGANESE REDOX REACTIONS: RATES AND MECHANISMS

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The objectives of my thesis research were to examine the dynamics of manganese redox reactions in nature and, as such, to assess the role that microorganisms play in mediating these processes. This was done using geochemical and microbiological techniques. A steady-state diagenetic model was developed that accounts for changes in porewater and solid-phase manganese profiles, as a result of advection, diffusion and redox reactions. The model was applied to two cores from the eastern equatorial Atlantic Ocean to estimate in-situ rates of manganese oxidation and reduction. The oxidation rates calculated are in good agreement with rates measured in laboratory experiments.

An in-situ dialysis technique was developed to examine chemical and bacterial rates of manganese binding and oxidation under diffusion-limited conditions in sediments. With this method, the microbial and abiotic components of manganese binding were quantitatively delineated in laboratory sediments spiked with manganese oxidizing bacteria. The abiotic removal of manganese by the same sediments has also been determined independently to define the relative importance of adsorption, ion exchange and autocatalytic oxidation in the removal of Mn^{2+} from solution. Independent measurements of bacterial and abiotic manganese binding were in good agreement with the diffusion-controlled rate data, validating the use of this technique as a means of examining manganese oxidation in situ.

Studies were undertaken on the reduction of manganates by inorganic species common in the marine environment. While nitrite and ammonia were found to be unreactive in reducing manganates, sulfide reacted extremely rapidly. Further studies on sulfide-mediated manganese reduction were performed using sulfate-reducing bacteria isolated from a nearby anaerobic mudflat. The results from these experiments indicated that in many marine environments the activity of these organisms may be important in indirectly reducing manganates.

Experiments were also performed to examine the direct involvement of bacteria in reducing manganates, using enrichment cultures isolated from coastal marine sediments. In the absence of oxygen, these enrichments reduced manganates when grown on either lactate, succinate or acetate in sulfate-free and sulfate containing artificial seawaters. Manganese reduction by these enrichment cultures occurred only under anaerobic conditions since cultures exposed to O_2 showed no ability to reduce manganates. Molybdate (a specific poison for sulfate-reducing bacteria) caused no inhibition of manganese reduction by these enrichments, while azide (an electron-transport inhibitor) caused an almost complete cessation of microbial manganese reduction. The addition of nitrate to the medium caused a slight decrease in the rate of Mn^{2+} production by these enrichments and, in one case, also caused a lag in the onset of manganese reduction. These findings are consistent with the hypothesis that

the manganese-reducing organisms in these enrichments use manganates as a terminal electron acceptor, and couple manganese reduction in some way to the oxidation of organic matter.

FORAMINIFERAL TRACE ELEMENTS:

UPTAKE, DIAGENESIS, AND 100 M.Y. PALEOCHEMICAL HISTORY

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Crustal generation rates from 80-110 m.y.b.p. have been suggested to be a factor two times those at present, from geological and geophysical evidence on eustatic sea levels, sea-floor magnetic lineations, and plate configurations. Other geophysical studies have suggested that crustal generation rates in the past have not been more than about 20% larger than those at present. Faster crustal generation should result in increased chemical fluxes to the ocean from hydrothermal circulation. The oceanic balance of Li is dominated by hydrothermal input; oceanic Li concentrations in the past could have been as much as a factor of two higher than those at present. This thesis investigates the history of oceanic Li concentrations over the last 100 m.y. to add independent geochemical evidence to the debate on sea-floor spreading rate variations.

Li/Ca ratios in the calcite shells of planktonic foraminifera were used in this study to determine oceanic Li/Ca ratios. The elemental uptake from seawater and the diagenetic changes in the sediment of foraminiferal calcite were investigated to assess the utility of these shells as indicators.

Laboratory culture experiments on planktonic foraminifera showed that Li, Sr, and Mg elemental ratios to Ca in foraminiferal shells are directly proportional to seawater ratios. The mean distribution coefficients determined in this study for foraminiferal calcite were: Li, $(5.2 \pm 0.6) \times 10^{-3}$; Sr, 0.16 ± 0.02 ; and Mg, $(0.89 \pm 0.18) \times 10^{-3}$. For Na, the ratios in foraminiferal shells did not vary in response to changes in seawater-solution Na/Ca ratios. Planktonic foraminifera were cultured in the laboratory at different temperatures to investigate the effect of temperature on the trace-element composition of foraminiferal shells. From these experiments, the interspecific differences in Sr/Ca, Mg/Ca, and Na/Ca ratios of foraminiferal calcite cannot be due solely to differences in calcification temperatures.

Li/Ca, Sr/Ca, Mg/Ca, and Na/Ca ratios were measured in planktonic foraminiferal shells from five DSDP sites; sample ages extended to 100 m.y. The effect of diagenesis on foraminiferal calcite composition was considered from a simple model comparing the composition of the foraminiferal calcite with that of inorganic calcite in equilibrium with the present-day interstitial water. From these comparisons, some foraminiferal calcite appeared to be in inorganic equilibrium with the interstitial water. For other samples, the comparison of the various indicators showed that these foraminiferal shells may be substantially unrecrystallized. Quantification of diagenetic changes in foraminiferal calcite chemistry is hampered by the lack of knowledge about inorganic calcite distribution coefficients applicable to sedimentary recrystallization reactions. The open-system nature of the chemical balances between sediments and interstitial water must be explicitly included in dia-

genetic models of changes in the chemical composition of foraminiferal calcite. As an example, the effect of recrystallization on oxygen-isotopic records of foraminiferal calcite is determined in a model with typical interstitial water oxygen isotope gradients.

From a Li mass balance model and the paleochemical records, the possible variations in crustal generation rates over the last 100 m.y. were evaluated. Alternate global extrapolations of the importance of hydrothermal circulation to oceanic mass balances, temporal changes in river fluxes of Li, the nature of the processes removing Li from the ocean, and the potential of coupled variations in the cycles of Ca and Li were considered with this model. This study concludes that at no time in the past 100 m.y. have oceanic Li concentrations been significantly greater than those at present. This geochemical evidence suggests that hydrothermal fluxes and sea-floor spreading rates from 80-110 m.y. were not significantly greater than those at present.

THE ECOLOGY AND ULTRASTRUCTURE OF MARINE MANGANESE-OXIDIZING BACTERIA

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As calculated from chemical models, the residence time of dissolved manganese (Mn^{2+}) at the U_2/H_2S interface in Saanich Inlet, British Columbia, Canada, was orders of magnitude shorter than purely inorganic mechanisms would predict; thus, biological catalysis was hypothesized by Emerson. The objectives of this thesis were (1) to test the hypothesis that bacteria mediate Mn^{2+} oxidation in such U_2/H_2S stratified marine environments, and (2) to establish mechanisms for bacterial Mn^{2+} precipitation. A method was developed to measure biological Mn^{2+} binding in the environment: water samples were incubated with radioactive $^{54}Mn^{2+}$ with or without poisons (shown in control experiments not to interfere in the chemistry of manganese), filtered as a function of time through 0.2 μ m membrane filters, and the percentage of radioactivity trapped on the filters determined. Such methods demonstrate that bacteria in Saanich Inlet significantly enhanced the rate of Mn^{2+} precipitation in a region just above the U_2/H_2S interface, but below the euphotic zone.

A second stratified environment, Framvaren Fjord, Norway, in which the interface occurs in the euphotic zone, was also examined. Binding experiments with $^{54}Mn^{2+}$ and $^{57}Co^{2+}$ were performed in dark incubations, with and without DCMU or azide in the light, and under air-saturating or oxygen-limiting conditions. $^{57}Co^{2+}$ and $^{54}Mn^{2+}$ precipitation were also measured in the presence of exogenous additions of Co^{2+} and Mn^{2+} . Phototrophic and lithotrophic organisms mediate Mn^{2+} and Co^{2+} binding. The rates are fastest under air-saturating conditions, as would be expected if higher U_2 concentration favors increased metabolic activity. A 3-fold increase in Mn^{2+} inhibits Mn^{2+} and Co^{2+} binding, and the addition of Co^{2+} (25- to 250-fold above ambient) has little effect on Mn^{2+} precipitation, but severely inhibits the Co^{2+} binding. Evidently, higher Co^{2+} and Mn^{2+} concentrations inhibit biological binding instead of increasing adsorption and autooxidation of these metals, as would be expected if inorganic processes were occurring. Measurements of the oxidation state of the material trapped on membrane filters established that Mn^{2+} was being oxidized and not simply bound.

In-situ Mn^{2+} binding rates were also measured in Saanich Inlet using a sampler incubation device (designed by C. Taylor, Woods Hole Oceanographic Institution) and gave results comparable to the published values of residence times for Mn^{2+} at the U_2/H_2S interface. Radioisotopes Fe^{3+} , Cd^{2+} , Mn^{2+} , Co^{2+} , Ni^{2+} and Zn^{2+} were also used in binding experiments in water samples from Saanich Inlet. Co^{2+} , Mn^{2+} and Ni^{2+} binding are all microbially mediated in the particulate layer above the interface.

Transmission electron microscopy of pure cultures of manganese-oxidizing bacteria and their laboratory-formed precipitates and of bacteria in the particulate layer of Saanich Inlet and on surfaces of manganese nodules from Uneida

Lake, New York was performed. Mn^{2+} precipitation by bacteria occurs in association with extracellular polymers (polysaccharides), capsules, sheaths or the surfaces of spores.

LABORATORY SIMULATIONS OF PETROLEUM-FORMING PROCESSES:
AN ISOTOPIC COMPARISON OF HIGH-TEMPERATURE PYROLYSIS AND CATALYSIS

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Laboratory simulations of the processes involved in the formation of petroleum were examined by stable carbon-isotope studies of five cryogenic distillation fractions of the gases produced by thermal treatment of organic substrates. Simple heat treatment of the substrate was contrasted with heat treatment in the presence of nickel and vanadium sulfides, ammonia, and water. Further simulations were performed to examine the effects of clay minerals and carbonates on the isotopic composition of the five distillation fractions. Plots of stable carbon-isotope ratio versus distillation temperature, for a variety of substrates representing marine and terrestrial organic matter, were compared with literature values for natural petroleum accumulations, and to the pyrolysis of Green River oil shale.

Pyrolysis reactions produced gases whose stable isotope ratios increased with increasing distillation temperature. For the methane fraction of these gases, the values ranged from -50‰ for oil shale, to -34‰ for plankton isolated from natural waters. The general structure of the substrate, and its initial isotope ratio influenced the carbon isotope ratios of the gases produced.

For the thermocatalytic production of gases, in the presence of nickel and vanadium sulfides, the carbon-isotope ratio of methane was apparently controlled by the substrate/catalyst ratio. At low substrate/catalyst ratios, isotopically heavy methane resulted, indicating a carbonium ion cracking mechanism. As the substrate/catalyst ratio was increased, methane carbon isotope values became more negative, to the point that thermocatalysis became indistinguishable from pyrolysis isotopically, suggesting poisoning of the catalyst. The gases produced in these reactions resemble those from geochemically immature environments.

Simulation reactions involving sedimentary constituents, such as clays and carbonates, exhibited a narrower and heavier range of isotope ratios, suggestive of a mature geochemical environment. The organic carbon content (analogous to the substrate/catalyst ratio) was important in determining the isotopic distribution of the gases in this type of simulation reaction. At low organic carbon content, on the order of those found in petroliferous rocks, methane was isotopically heavy, apparently resulting from a carbonium ion cracking mechanism. As the organic carbon content was increased, there was an apparent shift to a free radical cracking mechanism, as evidenced by greater isotopic fractionation between the substrate and the gases, and the increase in stable carbon isotope ratio with distillation temperature.

Based on stable carbon isotope studies of the hydrocarbon gases produced, it was possible to develop simulations of the reactions involved in the formation of petroleum in the marine environment.

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